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(54) Manufacturing a ceramic membrane.

(57) A method of manufacturing a ceramic membrane comprising a mesoporous support and a microporous top layer, which method comprises forming a coating solution comprising a silicon alkoxide, water, acid and alcohol; contacting the porous support with the coating solution; drying the coated support; and calcining the dried coated support, wherein the concentration of the silicon alkoxide in the coating solution is in the range of from 0.01 to 0.20 mol/l.

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The present invention relates to manufacturing a ceramic membrane comprising a mesoporous support and a microporous top layer.

In the specification and in the claims the expression "mesoporous support" is used to refer to a support having pores with a diameter in the range of from 3 to 5 nm (nanometer) and the expression "microporous top layer" is used to refer to a top layer having pores with a diameter smaller than 2 nm.

A ceramic membrane comprising a mesoporous support and a microporous top layer is disclosed in R.J. Uhlhorn, Ceramic Membranes For Gas Separation, Thesis University of Twente, the Netherlands, ISBN 90-9003618-0, 1990.

It is an object of the present invention to provide a method of manufacturing a ceramic membrane having a microporous top layer which is thin and substantially free from defects.

To this end the method of manufacturing a ceramic membrane comprising a mesoporous support and a microporous top layer according to the present invention comprises forming a coating solution comprising a silicon alkoxide, water, acid and alcohol; contacting the mesoporous support with the coating solution; drying the coated mesoporous support; and calcining the dried coated support, wherein the concentration of the silicon alkoxide in the coating solution is in the range of from 0.01 to 0.20 mol/l (mol/litre).

The coating solution according to the present invention contains a polymerized alkoxide which is believed to be formed in two stages, a hydrolysis stage and a condensation stage. In the hydrolysis stage the alkoxide is partly hydrolyzed in the presence of water to form a polymerizable species which condenses in the condensation stage to form the polymerized alkoxide.

It was found that when using a diluted coating solution a thin layer can be deposited and that drying is then so fast that undesired continuation of the condensation reaction is avoided. A further advantage of the method is that the coating can be applied in one step.

The following example illustrates manufacturing a ceramic membrane according to the present invention.

Admix 21 ml (millilitre) of tetraethyl orthosilicate ($Si(OC_2H_5)_4$) to 21 ml ethanol, and add 8 ml of 1 mol/l of HNO_3 and 3 ml water. Allow the mixture to react for three hours to obtain a solution of a polymerized silicon alkoxide. Add 5 ml of the solution of polymerized silicon alkoxide to 90 ml ethanol to obtain a coating solution.

Dip a standard alumina membrane (porosity 50 % and pore diameter 3 nm) in the coating solution to get a coated membrane. And heat the coated membrane at 25 °C/hour to 400 °C, followed by calcining the coated membrane at 400 °C for three hours and cooling the calcined membrane at 25 °C/hour.

The separation performance of a ceramic membrane manufactured according to the above method was evaluated as follows. The membrane was included in a membrane unit having a feed inlet, a retentate outlet and a permeate outlet. To the feed inlet a feed mixture was supplied at a temperature of 200 °C and at a pressure of 1.7 bar (absolute). The composition of the feed mixture is 50 % by volume H_2 and 50 % by volume CH_4. The permeance of H_2 was 125 $Nm^3/m^2/day/bar$ (wherein Nm^3 is standard cubic meter), the permeance of CH_4 4.3 $Nm^3/m^2/day/bar$ and the selectivity of H_2/CH_4 was 29.

Using a less diluted coating solution, for example a coating solution in which the concentration of the silicon alkoxide in the coating solution is about 0.4 mol/l it was found that the magnitude of the permeances and of the selectivity corresponded to the values for the mesoporous support which indicates that the top layer has defects.

The invention also relates to manufacturing a ceramic membrane having a top layer further comprising a metal, wherein to the coating solution had been added additionally an alkoxide selected from aluminium alkoxide, titanium alkoxide and zirconium alkoxide.

Suitably the silicon alkoxide is tetraethyl orthosilicate ($Si(OC_2H_5)_4$), the alkoxide can furthermore be tetra-n-butoxysilane ($Si(OC_4H_9)_4$) or tetra-(2-ethylbutoxy)silane ($Si(OC_6H_{13})_4$). The aluminium alkoxide is suitably aluminium sec-butylate ($Al(OC_4H_9)_3$) or aluminium isopropylate ($Al(OCH(CH_3)_2)_3$); the titanium alkoxide is suitably butyl titanate ($Ti(OC_4H_9)_4$), the alkoxide can furthermore be tetraisopropyl titanate ($Ti(OCH(CH_3)_2)_4$); and the zirconium alkoxide is suitably zirconium tetra-n-butylate ($Zr(OC_4H_9)_4$), the alkoxide can furthermore be zirconium tetra-n-propylate ($Zr(OC_3H_7)_4$).

As alkoxides can react with enols to give chelates with elimination of water, such chelates can be used as well. The expression "alkoxides" as used in the specification and in the claim is used to refer as well to alkoxides and to chelates formed by the reaction of the alkoxide and an enol such as 2,4-pentanedione. It will be understood that the chelate-forming reactant can be in the keto form, an example of such a reactant is acetoacetic ester.

The alcohol is suitably ethanol, other suitable alcohols are methanol, butanol and propanol.

The acid is suitably an inorganic acid, for example HNO_3, HCl or H_2SO_4.

The mesoporous support is suitably from an inorganic material, such as alumina, zirconia or porous glass.

Suitably the concentration of the alkoxides in the coating solution is in the range of from 0.01 to 0.20 mol/l, and in the coating solution the molar ratio of water to alkoxide is in the range of from 2 to 15 and the molar ratio of H^+ to metal is in the range of from 0.01 to 0.10.

Claims

1. A method of manufacturing a ceramic membrane comprising a mesoporous support and a microporous top layer, which method comprises forming a coating solution comprising a silicon alkoxide, water, acid and alcohol; contacting the mesoporous support with the coating solution; drying the coated mesoporous support; and calcining the dried coated support, wherein the concentration of the silicon alkoxide in the coating solution is in the range of from 0.01 to 0.20 mol/l.

2. The method according to claim 1, furthermore comprising adding to the coating solution an alkoxide selected from the group including aluminium alkoxide, titanium alkoxide, and zirconium alkoxide.

3. The method according to claim 2, wherein the concentration of the alkoxides in the coating solution is in the range of from 0.01 to 0.20 mol/l.

4. The method according to any one of the claims 1-3, wherein in the coating solution the molar ratio of water to alkoxide is in the range of from 2 to 15.

5. The method according to any one of the claims 1-4, wherein in the coating solution the molar ratio of H^+ to metal is in the range of from 0.01 to 0.10.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2701

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	CHEMICAL ABSTRACTS, vol. 108, no. 14, 4 April 1988, Columbus, Ohio, US; abstract no. 117659, page 338 ; * abstract * & PATENT ABSTRACTS OF JAPAN vol. 12, no. 96 (C-484)(2943) 29 March 1988 & JP-A-62 227 421 (SHIMADZU CORP) 6 October 1987 * abstract *	1	B01D71/04 B01D71/02
A	JOURNAL OF MEMBRANE SCIENCE vol. 44, no. 2/3, June 1989, pages 289 - 303 A. LABOT ET AL. 'SILICA MEMBRANES BY THE SOL-GEL PROCESS'		
A	DE-A-3 628 948 (MAN TECHNOLOGIE GMBH)		
A	EP-A-0 425 252 (WINSCONSIN ALUMINI RESEARCH FOUNDATION)		TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	EP-A-0 248 748 (CENTRE MERIDIONAL D'ENOLOGIE)		B01D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04 MAY 1993	DEVISME F.R.

CATEGORY OF CITED DOCUMENTS

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